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The Hydration of Isoprene with a Cation Exchange Resin Catalyst

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The direct hydration of isoprene using a cation exchange resin catalyst afforded α,α- and γ,γ-dimethyl allyl alcohols, together with some other products. The reaction schemes were also discussed.

INTRODUCTION

The hydration of terpenoid hydrocarbons to the corresponding alcohols would be a very important reaction from the viewpoint of industrial chemistry. There are many studies on the hydrolysis of the halides or the esters obtained from the terpenoids, but only few reports[1,2] are known about the direct hydration, especially in which cation exchange resins were used as catalysts. Polyanskii and Kozlova[1] reported hydration of isoprene in the presence of a cation exchange resin (KU-2), but they did not describe the reaction products and the reaction schemes in details. Their report prompted us to study the catalytic direct hydration of isoprene (a hemiterpene) using a cation exchange resin (Amberlite IR-120).

EXPERIMENTAL

Reaction Procedures. For example, in a 100 ml-autoclave, 20 g of purified isoprene (I) and 35 g of water were heated in the presence of 10 g of IR-120** with a small amounts of hydroquinone at a fixed temperature for a fixed period. Then the reaction mixture was cooled to room temperature, the catalyst was filtered off, and the organic layer was separated. It was dried over anhydrous sodium sulfate. The products were analyzed by glc (PEG 20 M/Celite 545, 4 mmϕ × 2.5 m, 100°C, H_2: 40 ml/min), and identified by means of ir, pmr, and so on, after the glc fractionations of them. IR-120 used in the reaction was dipped in 2N-hydrochloric acid, washed thoroughly with water and dried at 80°C before use.

Identification of the Products. A typical glc of the products was shown in Fig. 1. The data of ir, pmr and glc of each compound in peaks 1–10 agreed with those of the authentic samples, and each was identified as isoprene (I), α,α-dimethyl allyl alchohol (II), γ,γ-dimethyl allyl alcohol (III), 1,4-dimethyl-4-vinylcyclohexene-1 (IV),

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** The cation exchange resin (Amberlite IR-120) is abbreviated as IR-120.

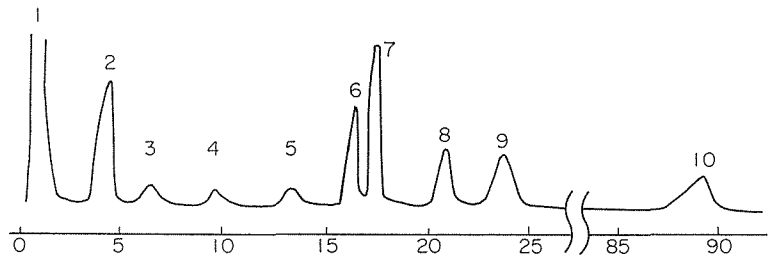

Fig. 1. A typical glc of the reaction mixture.
(90°C, 4 hours in Table 1.)

α,α-dimethyl allyl-γ,γ-dimethyl allyl ether (V), α-terpinene (VI), dipentene and/or diprene (VII) which was described in the next part, γ-terpinene (VIII), terpinolene (IX), and α-terpineol (X).

Analyses of Methyl Isopropenyl Cyclohexenes. In various reactions of isoprene, it has been reported that the reaction products often contain dipentene and/or diprene.[3] Since both compounds show the same glc, ir and pmr, it is very difficult to distinguish each other. The authors attempted the catalytic dehydrogenation of dipentene (A), which was obtained from α-pinene,[4] and that of a mixture of dipentene and diprene (B), which was obtained from isoprene on standing for several months,[5] in the presence of platinum-asbestos.[6] In the pmr spectra of the dehydrogenated products from (A) and (B), the signals at the high field were the same but those at the low field widely differ from each other, namely the product from (A) showed a single peak at 7.01 ppm but the product from (B) showed multiple peaks at 6.5–7.3 ppm. Moreover, in the ir spectrum of the latter, the absorption at 850 cm^{-1} was larger than those at 780 and 700 cm^{-1}, and the absorption band at 1700–2000 cm^{-1} was assigned to 1,3-substituted benzene.[7]

The above method was applied to the so-called dipentene fractions, and it was confirmed that the fractions contained mainly dipentene and a very small amounts of diprene.

RESULTS AND DISCUSSION

Hydration without Solvent. The results of the hydration of isoprene without solvent were listed in Table 1. From these results, (II) and (VII) seemed to be the initial products in this reaction. In order to study the reaction scheme in details, the reactions of (II) and (VII) with water and of (I) and (VII) without water were studied (Table 2 and 3). From these results, (I) was initially hydrated to the tertiary alcohol (II), and (II) rearranged to (III). It had been already confirmed that these alcohols were transformed into the ether (V) through the intermolecular dehydration,[8] and that isoprene easily dimerizes to the monoterpene hydrocarbons[9] (Table 3). The reaction schemes were summerized in Fig. 2. Polyanskii and Kozlova[1] reported that the reaction of isoprene with water by the action of KU-2 resin presumably afforded linalool as main product which was identified by the ir spectrum of the reaction mixture. On the contrary, in the author's experiments the formation of only trace amounts of linalool was confirmed.

Table 1. Hydration of Isoprene (I) without Solvent.
(I: 20 g, water: 35 g, IR-120: 10 g)

Temp. (°C)	Period (hr)	Conversion[a] (%)	Products[b] (percent on glc)									
			(II)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)	(IX)	(X)	others
70	1	2	70	5	—	—	—	10	—	—	—	15
80	1	4	50	5	3	—	3	13	5	7	—	14
90	1	4	45	3	2	—	5	20	8	6	—	11
100	1	5	40	3	3	—	5	20	10	8	3	8
120	1	10	25	—	2	4	5	30	8	5	14	7
75	3	5	40	5	2	—	6	16	13	12	5	1
100	3	7	34	4	2	3	5	22	9	10	10	1
120	3	15	8	—	5	2	15	17	20	18	12	3
90	4	6	30	2	2	2	10	20	12	15	7	—
100	4	8	22	2	2	2	18	20	10	10	9	5
110	4	20	7	—	2	4	18	20	9	8	12	20
75	9	12	18	—	2	3	14	8	10	7	15	23
100	12	28	10	—	2	3	8	18	12	10	14	23
120	8	40	5	—	—	3	20	20	8	6	9	29

a) Calculated from the amounts of unreacted isoprene on glc.

b) (II): α,α-dimethyl allyl alcohol, (III): γ,γ-dimethyl allyl alcohol, (IV): 1,4-dimethyl-4-vinyl cyclohexene-1, (V): α,α-dimethyl allyl-γ,γ-dimethyl allyl ether, (VI): α-terpinene, (VII): dipentene, (VIII): γ-terpinene, (IX): terpinolene, (X): α-terpineol, others: sum of the very small components (up to 2% on glc).

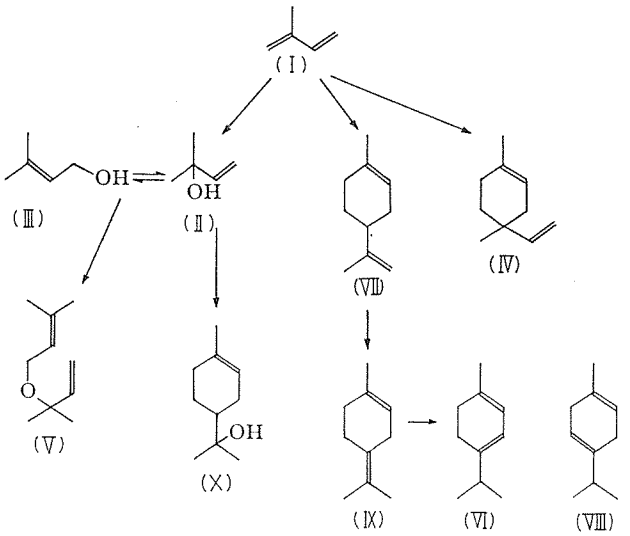

Fig. 2. The reaction scheme.

Table 2. The Reaction of (II) and (VII) with Water.
(Sample: 8 g, water: 30 g, IR-120: 10 g, 4 hours)

Sample	Temp. (°C)	Conversion (%)	Products (percent on glc)							
			(III)	(V)	(VI)	(VII)	(VIII)	(IX)	(X)	others
(II)	75	78	10	30	12	6	8	10	9	15
(II)	100	90	15	20	10	4	7	7	20	17
(II)	120	93	12	24	12	3	12	10	15	12
(VII)	100	53			40		24	27		9

Table 3. The Reaction of (I) and (VII) without Water.
(IR-120: 10 g, 4 hours)

Sample (g)	Temp. (°C)	Conversion (%)	Products (percent on glc)					
			(IV)	(VI)	(VII)	(VIII)	(IX)	others
(I) (20)	100[a)]	3	10	—	85	—	—	5[b)]
	75	48	5	18	12	28	15	22
	100	85	4	25	7	20	15	29
	110	88	5	33	4	12	15	31
	50[c)]	40	5	22	20	25	18	10
(VII) (8.5)	75	42		33		33	28	6
	100	70		41		24	27	8
	110	77		49		21	23	7

a) IR-120 was not used. The product (VII) contained a large amounts of diprene.
b) The main part of this fraction was confirmed to contain 1,5-dimethylcyclooctadiene-1,5 by means of ir and pmr.
c) IR-120: 20 g, 24 hours.

Table 4. Hydration of (I) in the Solvent (THF)
(I: 10 g, water: 5 g, IR-120: 5 g, THF: 15 g)

Temp. (°C)	Period (hr)	Conversion (%)	Products (percent on glc)									
			(II)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)	(IX)	(X)	others
80	4	3	54	18	—	3	—	15	3	—	—	7
100	4	5	57	22	—	3	—	11	4	—	—	3
110	4	6	53	19	—	3	3	15	5	—	—	2
80	10	7	60	16	2	3	2	5	5	3	—	4

Hydration with Solvent. The reactions of (I) with water in THF solvent were studied and the results were listed in Table 4. Without the solvent, the conversions increased with increasing temperature but the yields of alcohols decreased. On the other hand, when the solvent was used, the conversions and yields of alcohols were not influenced seriously with increasing temperature, and even if the reaction was carried out for a long period, the yields of the produced hydrocarbons were not so large. Moreover, the temperature slightly affected the ratios of the alcohols to the hydrocarbons. From these results, the hydration using a solvent is considered to be an effective method.

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